

A COMPARISON OF THE ACOUSTIC MOBILITY AND THE ELECTROPHORETIC MOBILITY OF COAL DISPERSIONS

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INTRODUCTION

Aqueous coal dispersions play a major role from mining to the utilization of coal. The properties of these dispersions, such as stability towards aggregation, rheology, etc., are controlled by two major factors, namely, the particle size and interfacial chemistry. The interfacial chemistry is controlled by the interactions of the coal surface with the aqueous phase.

Coal surface-aqueous phase interactions are controlled by rank, mineral content, surface functional groups, pore structure, adsorption, pH, ionic strength, etc. These interactions can be probed using electrokinetic techniques (1-11). Electrokinetic techniques presently used to investigate aqueous coal dispersions include microelectrophoresis and streaming potential (12). Although both of these techniques are invaluable to study coal surface interactions they cannot be used for process condition dispersions. As a result, questionable extrapolations to process conditions must be performed.

Below, we describe a new electrokinetic technique that utilizes ultrasonics and preliminary data on the application of this technique to coal dispersions. The advantage of ultrasonics are (i) virtually any particle size can be used from ions to aggregates, (ii) any concentration of the dispersed phase can be used from the ppm range to volume filling networks, (iii) samples can be optically opaque or photosensitive, and (iv) measurements can be made on flowing systems.

THEORY

In 1933, Debye (13) predicted that subjecting an electrolytic solution to a sound wave of ultrasonic frequencies would result in an alternating potential, the IVP or ion vibration potential, having the same frequency as the sound wave. The potential is detected with two electrodes placed normal to the sound propagation separated by a phase distance other than an integral multiple of the wavelength; the optimum separation being $(2n+1) \lambda/2$. The basis of the "Debye effect" is that the effective masses and frictional drag coefficients of anions and cations are different due to composition and solvation. These differences result in different degrees of displacement amplitude and phase. The relative displacement of anion and cation produces a separation of charge centers creating a vibrating dipole. The original theory of Debye has since been modified (14) and experimentally verified, a review of which can be found in reference (15).

In 1938, Hermans (16) and Rutgers (17) reported an effect similar to the Debye effect when ultrasonic waves were propagated through a colloidal dispersion. In contrast to the IVP where the displacement of anion

and cation produce an alternating potential, the relative displacement of a charged particle from its surrounding "ion atmosphere" induces the potential termed the colloid vibration potential or CVP. Since this time many colloidal systems have been investigated qualitatively using this technique (18-23). The first quantitative measurements were performed by Marlow et al (24) where the dilute theory of Enderby and Booth (25,26) is verified and extended to concentrates using the Levine et al (27) cell model theory.

Pictorially, the mechanism of the CVP is shown in Figure 1. To understand the mechanism of the CVP it is useful to point out that the CVP is analogous to the sedimentation potential or Dorn effect (28) and reflects the same intrinsic phenomena. Figure 1a shows a charged colloidal particle at rest with its accompanying "ion atmosphere" of "thickness" $1/\kappa$. If this particle is acted on by a gravitational field as shown in Figure 1b, the ion atmosphere is perturbed from equilibrium resulting in polarization and the formation of a static dipole. In contrast, if the particle is acted on by an acoustic field as shown in Figure 1c, a dynamic or vibrating dipole results. It is important to point out that in the Dorn effect the particle is caused to move relative to the medium but in the acoustic effect both particle and medium move and it is the relative motion that produces the effect.

As with the sedimentation potential, the acoustically produced dipole results in a potential that is immeasurably small for a single particle but a macroscopic measurable potential results in a swarm of particles such as in a colloid. Figure 2 shows the general technique used to measure the CVP. Two inert metal electrodes A and B are placed normal to the sound propagation and spaced at one-half a wavelength.

The relationship between the measured CVP and pertinent electrokinetic parameters for dilute aqueous dispersions ($\phi < 1$) can be expressed as (24)

$$CVP = \frac{2P\phi}{\lambda_0} \frac{(\rho_1 - \rho_2)}{\rho_1} \frac{\epsilon_0 D \zeta}{\eta} \quad [1]$$

where P is the sound pressure amplitude, ϕ the volume fraction of particles, λ_0 the conductivity of the medium, ρ_2 the particle density, ρ_1 the medium density, ϵ_0 the permittivity of free space, D the dimensionless dielectric constant, ζ the zeta or electrokinetic potential, and η the viscosity of the medium. Normalizing the CVP for P, λ_0 , ϕ , and $(\rho_2 - \rho_1)/\rho_1$ leads to an acoustic mobility AM having the same units as the electrophoretic mobility EM, i.e.,

$$AM = \frac{CVP \lambda_0}{2P\phi(\rho_2 - \rho_1)/\rho_1} = \frac{\epsilon_0 D \zeta}{\eta} = EM \text{ (m}^2/V_s) \quad [2]$$

Thus, measurements of the CVP, P, and λ_0 as well as knowledge of the relative particle density and concentration leads to the same information as obtainable from electrophoresis.

In concentrated dispersions particle-particle hydrodynamic and electrical interactions occur. Applying the Levine et al (27) cell model theory of the Dorn effect to the CVP results in an interaction parameter $F(\kappa a, \phi)$ on the right hand side of equation [1] where a represents the electrokinetic radius or the particle size a divided by the "thickness" of the ion atmosphere. Figure 3 shows a plot of the interaction parameter $F(\kappa a, \phi)$ as a function of ϕ for the case where $\kappa a \gg 1$ and $a > 0.5 \mu\text{m}$

which will invariably be the case in aqueous coal dispersions. Thus, instead of the CVP increasing linearly with ϕ as predicted by the dilute theory, the CVP will initially rise linearly and then gradually level off and go through a maximum.

EXPERIMENTAL

Materials

A bituminous coal used as a reference sample in previous work (29-32) obtained from General Motors Corporation was used in this work. The coal was air ground to 100% minus 200 mesh and stored in a sealed container. The ash content was 4.8%.

The water used was distilled and ion exchanged and had a specific volume conductivity of 2E-4 S/m . Solution acidity and alkalinity was adjusted with 1N KOH or 1N HCl obtained standardized from Fisher Scientific Company.

Methods

Aqueous coal dispersions were prepared by first outgassing the desired quantity of coal at 30 C under vacuum. The desired quantity of distilled water was then added by back filling under vacuum. The samples were then rolled in polyethylene containers for 24 hr on a mill. Five dispersions were prepared, namely, 0.04, 0.1, 0.2, 0.3, and 0.4 weight percent coal.

Acoustic measurements were performed with the Pen Kem System 7000 Acoustophoretic (tm) Titrator. The System 7000 measures the CVP, P , λ_0 , pH, T , and titrant volume accurate to 1 microliter. All measurements were performed at 25 C. A description of the apparatus can be found in reference (24). All pH titrations were performed by starting at the equilibrated pH and adding acid to one aliquot of sample and then base to another aliquot of sample and then combining the data.

Electrophoretic mobility measurements were performed with the Pen Kem System 3000 Automated Electrokinetics Analyzer some of which are reported in reference (11).

RESULTS AND DISCUSSION

The dependence of the CVP on GM coal concentration for a pH adjusted to 6.2 is shown in Figure 4. The CVP initially rises linearly with concentration and then levels off and goes through a maxima at a coal concentration of 30% by volume. Also shown in Figure 4, are the calculated values based on the dilute theory and cell model. These values were calculated by using measured values of the dispersions supernatant conductivity, particle density 1.22 g/cm³, and the particles electrophoretic mobilities determined by sampling the supernatant of the settled dispersions, all of which are given in Table 1. The high supernatant conductivities are the result of both dissolution of material from the coal and electrolyte added to adjust the pH to 6.2. The correlations shown in Figure 4, show good agreement between experiment and theory. Thus, ultrasonic electrokinetic measurements can be applied to concentrated coal dispersions to obtain meaningful information about the electrokinetic properties of the dispersion. Figure 5, shows a plot comparing both electrophoretic and acoustic mobilities as a function of pH for GM coal. The acoustic mobilities were obtained at a particle concentration of 4% whereas the electrophoretic mobilities were obtained by adding a few drops of this dispersion to a solution of the desired pH (11). Thus, the acoustic mobilities are

determined with an aqueous phase containing any leached materials whereas the electrophoretic data is taken with approximately a 200-fold dilution in the leached materials.

Good agreement is shown between electrophoresis and ultrasonics as shown in Figure 5 irrespective of the seemingly different preparation techniques. The mobility is positive below a pH=5.8, the isoelectric point Iep , and negative above this pH. Most researchers believe the negative potential at high pH is the result of the dissociation of carboxylics, phenolics, etc. on the coals surface (3,11) or alternatively due to the adsorption of metal hydroxides formed from the mineral present in coal (2). A positive potential below the isoelectric point is described as the result of protonation of the acid groups on the surface of the coal (10), the adsorption of cations (6), or the adsorption of hydronium ions (11).

Figure 6. shows a plot of the acoustic mobilities of GM coal as a function of pH at two particle concentrations, namely, 0.04 and 0.40% by volume. The behavior in the concentrated dispersion no longer resembles that obtained in the dilute dispersion. The mobilities at the higher concentration are generally lower, the isoelectric point is shifted to a significantly lower value, and maxima and minima are seen at high and low pH.

We believe that the concentration effect shown in Figure 6. results from the fact that in the concentrated dispersion the equilibrated supernatant conductivity is greater than in the dilute case. Thus, in the concentrate significantly more material is leached from the coal pores and surface. As a result, the double layer is compressed in the concentrate and the potentials accordingly lowered. Also, the dissolved materials of the coal become "specifically" adsorbed.

A shift to a lower pH as well as a maxima and a reversal of potential with lowering pH as shown in Figure 6. results from the chemisorption of anions (12). A maxima and reversal at high pH also seen in Figure 6. is the result of the adsorption of cations (12). Thus, in concentrated aqueous coal dispersions deviation of the electrokinetic properties from ppm studies will be significant. The deviations are the result of chemically adsorbed anions at low pH values and adsorbed cations at higher pH values. The adsorbed materials are produced from leaching of the coal surface and pores with subsequent deposition.

We believe that the results described above show that the application of ultrasonic electrokinetic techniques to aqueous coal dispersions will be of great practical significance in the future when attempting to characterize charged coal particles in concentrates.

Table 1. Comparison of cell model calculations of the CVP and experiment as a function of GM coal concentration at a pH=6.2.

Coal Volume Fraction	EM (m^2/Vs) $\times 10^8$	λ_0 (S/m)	F(ka, ϕ)	-CVP (mV)	
				Exp.	Cal.
0.04	-1.00	0.18	0.95	0.016	0.019
0.10	-0.97	0.18	0.88	0.049	0.042
0.20	-0.97	0.19	0.75	0.072	0.067
0.30	-0.96	0.21	0.63	0.074	0.078
0.40	-0.95	0.24	0.51	0.072	0.069

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Figure 1. Mechanism of Dorn effect and CVP

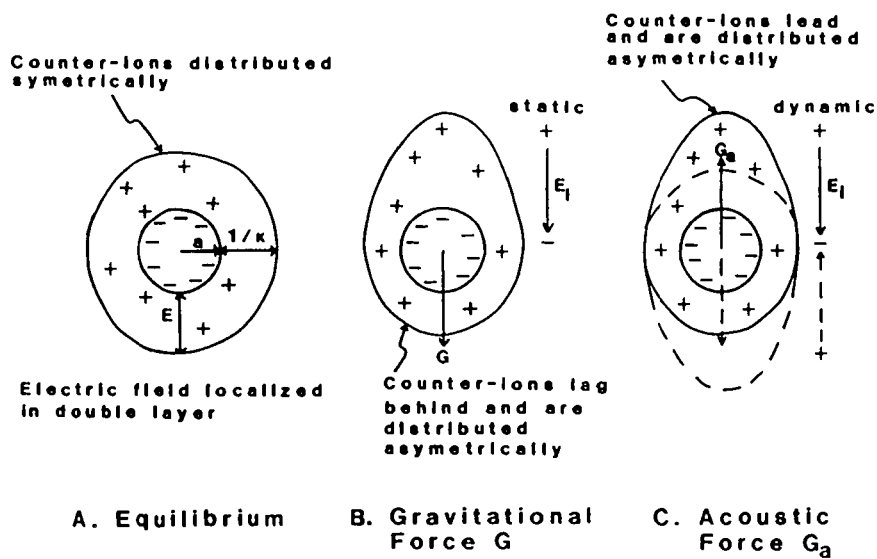


Figure 2. Measurement of CVP

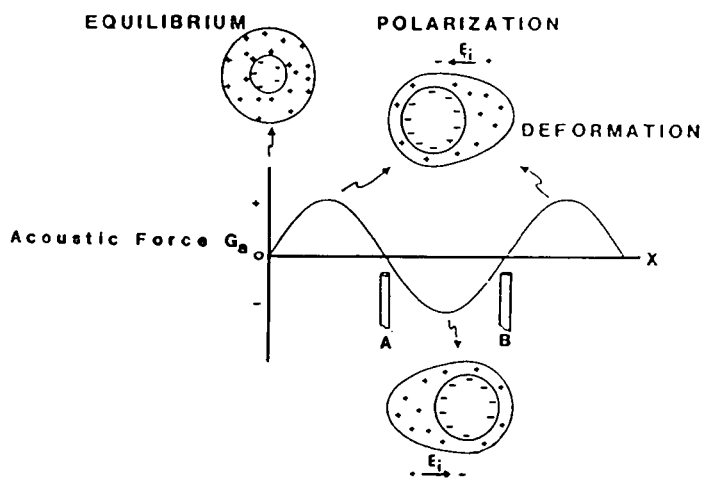


Figure 3. Interaction parameter as a function of volume fraction.

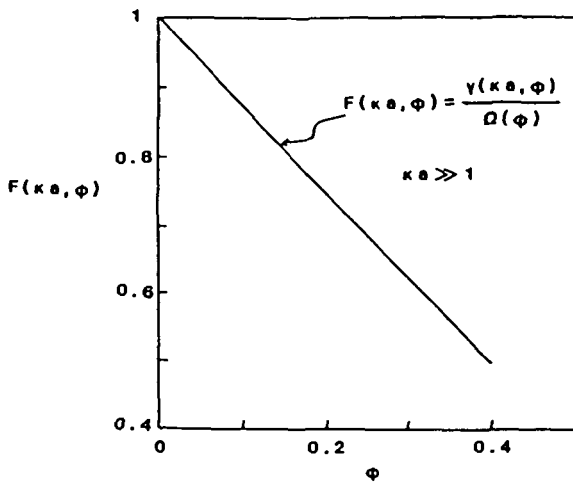


Figure 4. CVP as a function of coal concentration at a pH of 6.2.

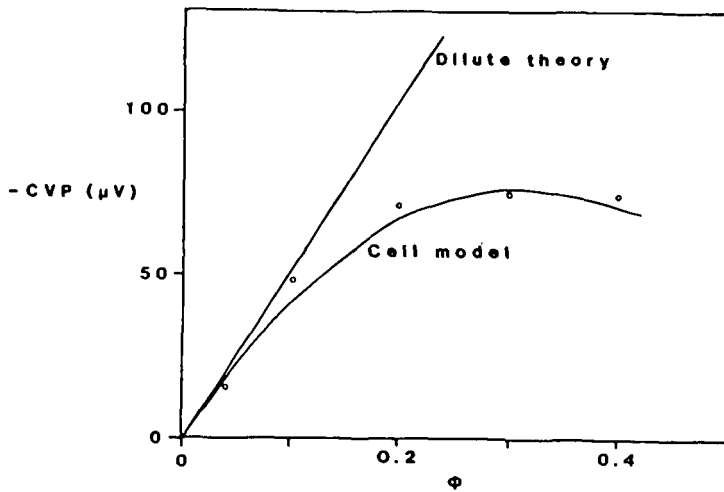


Figure 5. Comparison of acoustic and electrophoretic mobilities for GM coal.

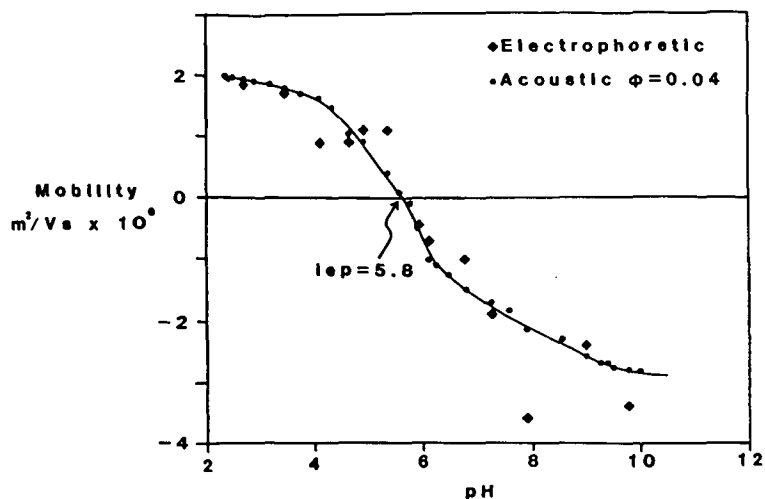


Figure 6. Effect of GM coal concentration on acoustic mobility.

